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Dyeing of Polyester Using Crude Disperse Dyes by Nanoemulsion Technique

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Abstract: In this study three types of nanodisperse dyes were prepared using oil in water nanoemulsions and applied on microdenier polyester fabric. Nanoemulsions were prepared by three methods: ultrasonication, phase inversion compositionand spontaneous emulsification process. Nano scale level emulsion was obtained by all the three methods evidenced by Dynamic Light Scattering method. The dyeing characteristics of micro denier polyester dyed with crude disperse dyes using these nanoemulsions and that dyed with commercial form of same dyes was compared. Dyeing of very high color depth was obtained using these nanoemulsions thus eliminating the requirement of milling of the crude disperse dye with the dispersing agent resulting in cost, time and energy savings.

Keywords: Nanodisperse dyes, Nanoemulsion, Dynamic Light Scattering, Polyester.

1. Introduction

The use of nanomaterials and nanotechnology-based processes is growing at a tremendous rate in all fields of science and technology. Textile industry is also experiencing the benefits of nanotechnology in its diverse field of applications. Textile based nano-products starting from nanocomposite fibers, nanofibers to intelligent high-performance polymeric nanocoatings are getting their way not only in high performance advanced applications but nanoparticles are also successfully being used in conventional textiles to impart new functionality and improved performance. Greater repeatability, reliability and robustness are the main advantages of nano technological advancements in textiles [1].

An emulsion is a system containing two immiscible phases, one of which is the dispersed phase as droplets (internal phase) and the other is the continuous phase (external phase) [2]. There are two types of emulsions: oil in water (o/w) or direct emulsions and water in oil (w/o) or indirect emulsions [3]. Nanoemulsions are fine oil-in-water dispersions, having droplet covering the size range of 100-600nm [4-5]. Nanoemulsions are also referred to as mini-emulsions [6-7].

Nanoemulsions can be prepared using two methods: high energy and low energy emulsification methods. High energy methods mainly include ultrasonic emulsification, high pressure homogenization, and microfluidization. The main principle behind these methods is application of a force/pressure which is higher than Laplace pressure so that the dispersed phase can be broken down to small molecules. In these methods, formation of such nanometric scaled droplets is governed by directly controllable formulation parameters such as the quantity of energy, amount of surfactant and nature of the components [8].

Low energy methods overcome the problem of considerable amount of energy required by high energy methods to prepare nanoemulsions. They make use of the physiochemical properties of surfactants and co-surfactants with the energy input of only a magnetic stirrer. There are three main methods under this category: Phase inversion temperature, Phase inversion composition and Spontaneous emulsification[9].

Disperse dyes are non-ionic dyes, having very limited solubility in water at room temperature and have substantively for one or more hydrophobic fibres such as Polyester (PET) and Polyamide (PA) [10]. They are usually applied from a fine aqueous dispersion containing some dissolved dye. It is the aqueous solution from which dyeing takes place, despite the low water solubility of the dye [11].In the textile processing industry, disperse dyes are used which contains 40 -60 % dispersing agent. The minimum size for disperse dyes should be 1 micron or less and it should withstand temperature up to 140^0C.The disperse dye size is reduced to 1 micron with the help of milling process. The milling procedure itself is a time and energy consuming procedure [12].

In this work an attempt has been made to provide a potential solution to alleviate the disadvantages involved in disperse dyeing of PET using nanoemulsions as a dyeing medium.

2. Material and Methods

2.1 Materials

PET fabric of 500gsm was provided by Piyush Syndicate, Mumbai, India. Coconut oil (Kerafed™) used in spontaneous emulsification method was procured from local market in Mumbai, India. Paraffin oil (density=0.86 at 25ºC, 99%), Acetone as a solvent, Dimethyl foramide as an organic solvent, and Acetic acid were of AR grade.

Sorbitanmonooleate (Span 80, chemically pure grade) as a lipophilic surfactant, Polyoxyethylene (20) sorbitanmonolaurate (Tween 20, chemically pure grade) as a hydrophilic surfactant in spontaneous emulsification method were supplied by Mohini Organics Pvt. Ltd., Mumbai.

Saragen 50 used as dispersing agent and Saragen KDFused as leveling agent were obtained from Sarex Chemical Ltd, Tarapur, India. Auxipon N P a nonionic soap was obtained from Auxichem Industires Ltd., Mumbai, India.

Particle Size Analyzer of Malvern, United Kingdom was employed to determine the droplet size of the particles. Three types of Crude dyes and same type of Commercial dyes were procured from Spectrum Dyestuffs Pvt. Ltd, Surat, India. The properties of the disperse dyes used in this study having three different energy levels are listed in the Table 1.

2.2 Methods

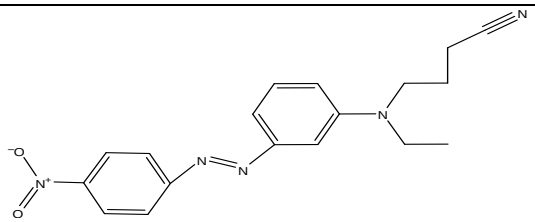
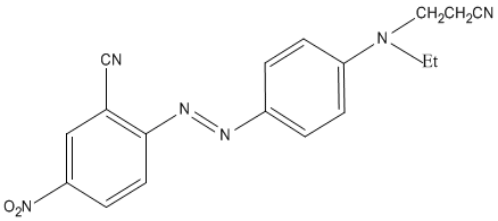
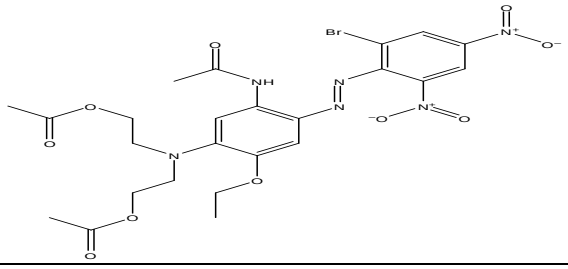
2.2.1 Preparation of Nanoemulsions

Nanoemulsions were prepared by three methods: Ultrasonication (SO), Spontaneous Emulsification (SE) and Phase inversion composition (PIC).

1. SO Method: 300 ml nanoemulsion was prepared by SO method using Leela Sonic 250 UPP Ultrasonicator (Leela Electronics) of power 250W and diameter probe 20mm [13]. 45ml of (15% v/v) paraffin oil, 16.8m of Tween 80 (5.6% v/v) and 238ml of distilled water (79.4% v/v) were premixed undermagnetic stirring for 5 minutes and then subjected to sonication for 15 minutes.

2. SE Method: The homogenous organic phase was prepared using 16grams of coconut oil as an oil phase, 3.4 grams of Span 80 as a lipophilic surfactant and 160ml acetone as water miscible solvent and is then vigorouslymixed. The aqueous phase is made by taking 320ml of distilled water and 5.4 grams of Tween20 as hydrophilic surfactant.

Table 1. Properties of Disperse Dyes:

Serial No.	Dye Name	Dye Structure	Energy Level	Molecular Weight (gm/mole)	Solid Content
1.	Orange 2 RLW 200% (C.I. Disperse Orange 25)		Low	323.35	37%
2.	Rubine 2 GFL 200% (C.I. Disperse Red 73)		Medium	348.35	51%
3.	Navy Blue 2 GP 200% (C.I. Disperse Blue 79.2)		High	639.4	61%

The organic phase was injected to the aqueous phase under constant magnetic stirring; the oil-in-water nanoemulsion was formed instantaneously by diffusion of the organic solvent in the external aqueous phase leading to the formation of nano size droplets. The magnetic stirring was maintained for 30 minutes to let the system reach equilibrium at room temperature. After that water-miscible solvent was allowed to evaporate for 45 minutes at 70˚C [14].

3. PIC Method: 400ml of nanoemulsion was prepared by PIC method. 10.78grams of Spam 80 and 9.22 grams of Tween 80 were dissolved into 20 grams of Paraffin oil under magnetic stirring. The surfactant-oil mixture and water were placed separately in a water bath at 60°C temperature. Then the water phase was added drop wise (2ml/min) to the oil solution. After the emulsification, the emulsified mixture was cooled immediately at room temperature by keeping it in chilled water (5ºC) [15].

2.2.2 Preparation of Nanodisperse Dye Solution

Required quantity of crude dyes were taken for 3% shade according to the solid content of the dyes obtained and were dissolved in 20ml Dimethyl foramide. This solution was added drop wise to 80ml nanoemulsion prepared. Thus 100ml of three dyes were prepared.

2.2.3 Preparation of Commercial Disperse Dye solution

Required amount of commercial dyes were measured and was added to 0.5 gpl of dispersing agent with 0.5 gpl of levelling agent. The solution was then properly mixed. 2-3 drops of acetic acid were added in the solution to adjust the pH in between 4-5 as the dyeing takes place in acidic conditions.

2.2.4 Solid Content of Crude Dye

5 gram samples of each dye were taken in a petridish and kept in an oven at 100ºC for three hours. The drying was carried out till constant weight was obtained. The solid content was calculated by knowing the weight of the samples before and after drying.

2.2.5 Dye Content in Finished Dye

The actual amount of disperse dye in commercial samples was found out by using UV-Visible spectrophotometer Techcomp 8500 (Shanghai, China). The commercial disperse dyes were dissolved in DMF and water (75:25 for finished disperse dye and 100% for Crude dye) mixture and the concentration was determined by noting the absorbance of the samples at maximum wavelength. The amount of dye in the commercial sample was then determined by using calibration curves of the respective crude dyes.

2.2.6 Dyeing of PET fabric

The PET fabric was first scoured with Auxipon NP followed by washing with tap water and then air dried. The fabric was cut into 2 grams of sample size and the PET fabric was dyed in Infra color dyeing machine of RBE Electronics, Mumbai, India with nano disperse dye and commercial disperse dye solution at 100, 110,120 and 130^0C for 60 minutes. The two varieties of crude disperse dyes taken in nanoemulsion form and the commercial ones were dyed at 3% depth of shade. The percentage shade taken for dyeing were based on the actual amount of dye present in the commercial dye and that of the crude dye in the wet cake so that we can compare the color value of the dyeing obtained using the nanoemulsions and that with the regular finished commercial dye. The dyed samples were then subjected for reduction clearing treatment for 20 min at 70°C with 2 g/l of caustic soda and 2 g/l sodium hydrosulphite. All fiber samples were then thoroughly washed at room temperature followed by neutralization with 1 g/l acetic acid solution. The fiber samples were finally washed in water and then air dried.

2.2.7 Evaluation of Color Strength

The samples were evaluated for color depth in terms of Kubelka Munk function (K/S) using a Spectra Flash® SF 300, Computer Color Matching system supplied by Data Color International, U.S.A[16-17] Kubelka Munk K/S function is given by:

$$\frac{K}{S} = \frac{(1-R)^2}{2R} \quad ,$$

Where, "R" is the reflectance at complete opacity,
"K" is the absorption coefficient,
"S" is the scattering coefficient.

2.2.8 Wash Fastness

The dyed samples were then subjected for washing fastness by ISO 3 method in a Launder-O-meter for 20 min at 60^0C, using 2 gpl non-ionic soap (Auxipon NP) and 2 gpl soda ash at a liquor ratio of 50:1[16-17].

2.2.9 Light Fastness

Light Fastness determined by ISO 105-A02 test method. Dyed fiber samples were exposed to light continuously for 17 hr.

2.2.10 Sublimation Fastness

The Sublimation Fastness was determined by AATCC 133-2009[18] test method.

3. Results and Discussion

3.1 Particle Size Analysis of Nanoemulsions

Figures 1, 2, 3 and Table 2 shows the particle size analysis of nanoemulsions prepared by three different methods. As seen in the figure, the droplet size of nanoemulsion obtained was least in the nanoemulsion prepared by PIC method with an average droplet size of 151.3nm. The largest droplet size was obtained in the nanoemulsion prepared by SO method. These results show that the droplet size of nanoemulsions prepared by PIC method is smaller than that prepared by SO method. The droplet size of the nanoemulsion prepared by SE method is more than PIC method. The reason could be that more time must be required to obtain less droplet size in the nanoemulsion prepared by SE method.

Table 2. Particle Size Analysis of Nanoemulsions prepared

Nanoemulsion Preparation Method	Average Particle Size (nm)
SO	244.3
SE	191.7
PIC	157.3

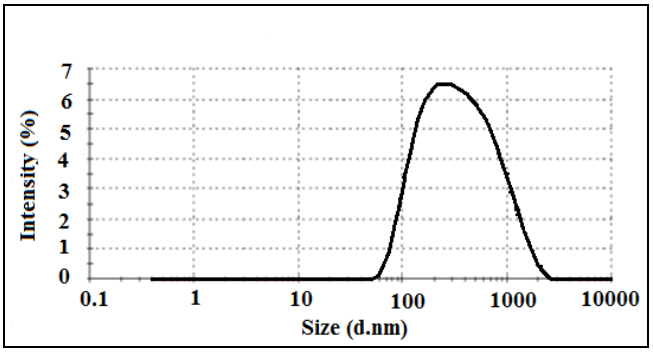


Figure 1.Particle Sixe Analysis of Nanoemulsion prepared by Ultrasonic Emulsification Method.

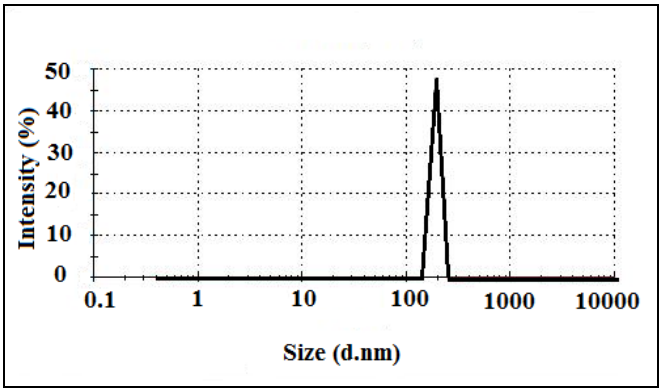


Figure 2. Particle Size Analysis of Nanoemulsion prepared by Spontaneous Emulsification Method.

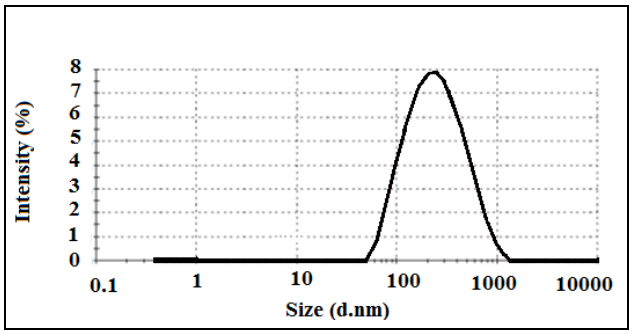


Figure 3. Particle Size Analysis of Nanoemulsion prepared by Phase Inversion Composition Method.

3.2 Dye Content in Finished Dye

Dye content in the finished dye is the amount of dye present (after subtracting the amount of dispersing agent added) in the commercial dye sample which was found out by using UV-VIS spectrophotometer and the values are given in Table 3.

Table 3. Active Content of Finished Dye

	C.I. Disperse Blue 79.2	C.I. Disperse Red	C.I. Disperse Orange
Active Dye Content	40%	44%	24%

3.3 Effect of Method of Preparation of Nanoemulsion on K/S Values

Figure 4, 5, and 6 gives the K/S value of C.I Disperse Orange, Red and Blue prepared by various nanoemulsion methods at different temperatures.

As seen from the above graphs, clearly the color values obtained by using nanoemulsions for dyeing are higher at all temperatures than those dyed by conventional disperse dyeing process. Similar results were obtained for other two dyes. Thus by using nanoemulsions for dyeing of microdenier PET, higher depths of color were obtained.

The reason for getting more depth is because nanoemulsions assist penetration of dye molecules in to the compact structure of polyester to a greater extent due to the nano metric size of the oil phase containing the dye molecues as against the commercial dyes whose size is always in micrometer range. Also the nanoemulsions prepared by SE method gave higher K/S values compare to PIC and SO methods. This could be explained on the basis of size again as too small size of the penetrating oil (obtained in PIC method) can enter the fine fibre structure easily but can also come out of it with the same ease hence the rate of penetration and desorption is same and the dye doesn't get that much effectively trapped inside the fibre. Whereas in case nano emulsion prepared by SO method the oil droplet size is biggest amongst the three methods and hence there is difficulty for the dye to penetrate inside the fibre.

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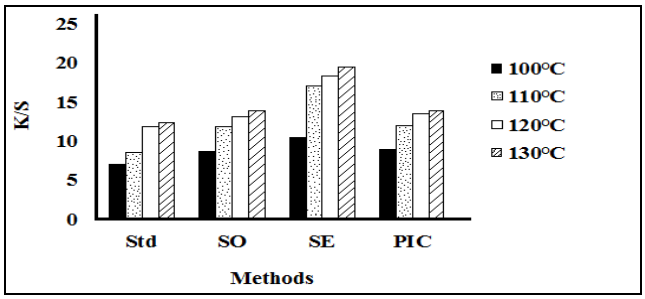

Figure 4. K/S of C.I Disperse Orange 25

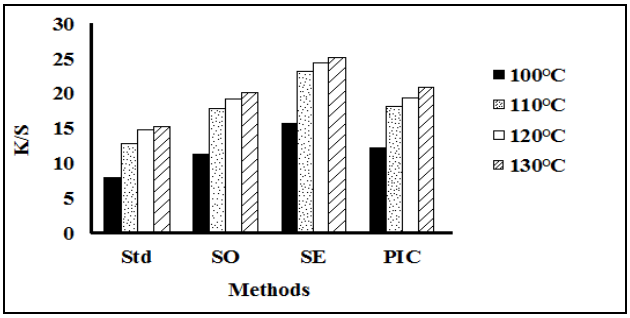

Figure 5. K/S of C.I Disperse Red 73

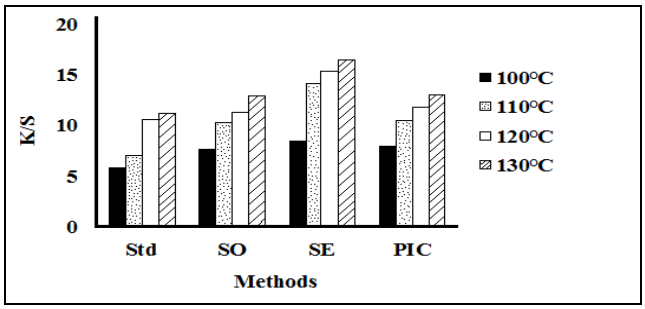

Figure 6. K/S of C.I Disperse Blue 79.2

3.4 Evaluation of Wash Fastness Properties

Table 4 to 6 gives the wash, light and sublimation fastness properties of nanodisperse dyes prepared using various nanoemulsion methods.

Table 4. Wash Fastness Properties of Nanodisperse dyes

Name of the Dye	Ultrasonic Emulsification	Spontaneous Emulsification	Phase Inversion Composition	Commercial Dye
Orange 25	5	5	5	5
Red 73	5	5	5	5
Blue 79.2	5	5	5	5

Table 5. Light Fastness Properties of Nanodisperse Dyes

Name of the Dye	Ultrasonic Emulsification	Spontaneous Emulsification	Phase Inversion Composition	Commercial Dye
Orange 25	8	8	8	8
Red 73	8	8	8	8
Blue 79.2	8	8	8	8

Table 6. Sublimation Fastness Properties of Nanodisperse Dyes (Temperature=210°C)

Name of Dye	Ultrasonic Emulsification	Spontaneous Emulsi-	Phase Inversion Composition	Commer-cial Dye
Orange 25	5	5	5	5
Red 73	5	5	5	5
Blue 79.2	5	5	5	5

We can see that the all fastness properties of the dyeings obtained by using all the three types nanoemulsions are at par or excellent with those that are obtained with commercial dyes using standard dyeing technique. This can happen only because the solid solution theory that is used to explain the dyeing of polyester with disperse dyes is applicable when the dyeing by nanoemulsion technique is used as it is only the form in which the dye is applied is different here otherwise the phenomena of dyeing is same.

4. Conclusion

In this work, conventional dyeing of microdenier polyester with disperse dyes have been replaced with dyeing using nanoemulsions. Nanoemulsions act as a transporting medium for the dye to penetrate into the fiber surface. The results obtained in this work illustrate that the color values of nanoemulsion assisted dyeing of polyester are higher than those of conventional dyed process which saves on a considerable amount of energy, time and money utilized in the conventional disperse dyeing of polyester. Also, the harm caused to the environment is minimized by dyeing of polyester using nanoemulsions. Therefore, this provides potential and a novel alternative for disperse dyeing of polyester.

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